

Experimental Study of the Mechanism of Film Formation*

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Synopsis

The temperature above which a polymer latex forms a continuous film, i.e., the minimum film formation temperature (MFT), was studied as a function of particle size, surface tension, and stiffness of the polymer. The MFT was found to occur in the region where the modulus of the polymer G is decreasing very rapidly with increase in temperature. The MFT appears to be independent of particle size but very strongly dependent on polymer stiffness. The random error in MFT measurement, however, is equivalent to a change in polymer modulus of the same order of magnitude as the particle size variation investigated. Thus the ratio Gr/γ , where r is the particle radius and γ the surface tension, may be constant as predicted by Brown for a given chemical composition but the instrumentation used was not sensitive enough to prove it. The value of that ratio, however, depends markedly upon chemical composition going from an average value of 0.58 for a nonpolar copolymer (75% styrene, 25% *n*-butyl acrylate) to an average value of 260 for a more polar copolymer (50% ethyl acrylate, 50% methyl methacrylate). The quantity $(\text{MFT}-T_g)$, where T_g is the glass temperature of the polymer, also depends upon the chemical composition going from a value of 10°C. to -3°C. when changing from the nonpolar copolymer to the more polar copolymer mentioned above.

INTRODUCTION

The use of polymer latices as binders in the paint, paper coating, and floor polish fields is large and expanding. Since these fields demand the formation of continuous films at the use temperature, it is becoming increasingly important to know the temperatures at which a particular latex will deposit a continuous film. Much research time could be saved if it were possible to predict this temperature on the basis of preparation variables. This would be possible of course if the correct mechanism of film formation were known in detail.

The mechanism of film formation is not only technologically important but is scientifically interesting and a number of attempts have been made to understand the physical mechanism operating. Henson, Taber, and Bradford¹ have proposed the mechanism to be that of the sintering of the parti-

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cles, following compaction and water loss, in a process in which the polymer surface tension provides the driving force and the polymer viscosity is rate determining.

Brown,² on the other hand, proposes that water evaporation from the capillaries in the surface of the partially dried emulsion is responsible for film formation. Following initial compaction of the particles into a close packed configuration as the result of water evaporation, it is proposed that the tensile strength and adhesion to the polymer of the interstitial water cause the polymer to be "pulled" into the void spaces as the water is moved to the surface under surface tension forces. Evaporation at the surface results in a continual flow of water to the surface. Film formation is accomplished if the viscoelastic properties of the polymer permit sufficient deformation to accomplish coalescence under the driving force available. Voyutskii³ proposes that Brown's model is too simple and does not consider some other facts that influence film formation such as the nature of the surfactant.

Barb and Mikucki⁴ believe that the large surface-to-volume ratios present in these colloidal systems free significant portions of the polymer chains from appreciable intersegmental interference. Therefore, when such a latex particle comes into contact with a surface of the same material the resultant freedom of molecular rotation permits surface interpenetration to occur, and a weld of finite mechanical strength is formed at temperatures below the second-order or glass temperature of the bulk material. Although they do not develop a quantitative theory from this picture, it is implied that the temperature at which such a weld is possible would be a function of the surface-to-volume ratio and should always be less than the second-order temperature of the bulk material.

There have been few experiments which can be called critical tests of the various models. An exception is the work of Talen and Hover,⁵ in which the film formation of poly(vinyl acetate) dispersions is investigated by means of stress-strain experiments on free films and electron micrographs of the film surface. Their conclusion was that Brown's concept explained the facts better than the mechanism of Henson et al. (Brown has also summarized² a number of objections to the mechanism of Henson et al.) Recently Protzman and Brown⁶ described an instrument which measures the temperature above which a latex forms a continuous film, i.e., the minimum film formation temperature, and quantitative investigations are now possible.

In this paper we describe some experiments utilizing the instrument of Protzman and Brown in the investigation of a number of latices having different particle sizes. Since Brown's theory predicts that at the minimum film formation temperature the quantity Gr/γ will be constant (where G is the modulus of the polymer at that temperature, r is the latex particle radius, and γ is the surface tension), and Barb's model predicts a dependence on the surface to volume ratio, we expected to ascertain which theory best represents the experimental facts. Although our results are somewhat

ambiguous, Brown's theory is most consistent with the data. We are in agreement, however, with Brown in that his theory is only a good first approximation and that other parameters such as the polarity of the polymer are important. We did not investigate the effect of changing emulsifier type, although Voyutskiy indicates that this also is an important variable.

EXPERIMENTAL METHODS

A. Minimum Film Formation Temperature Measurements

The minimum film formation temperatures (MFT) were obtained by the use of an apparatus described by Protzman and Brown.⁶ This apparatus essentially is an aluminum slab in which a constant and uniform temperature gradient is maintained. A latex to be measured is spread uniformly in one of several sample wells. The point at which the film becomes discontinuous when dry is observed and this temperature is recorded as the MFT. To insure that the films were actually continuous when formed above the MFT we scraped many of the films with a knife edge moving in the direction from low temperature to high temperature. Below the MFT the material chipped off the bar quite easily but above the MFT the coating would not lift off the bar. In addition the transition from easily chipped to strong coating took place at the visually observed MFT.

It has been shown that neither the amount of latex used nor the polymer solids in the latex affects the MFT value.⁶ The apparatus was kept in a constant temperature (23°C.), constant humidity (54% R. H.) room. Although most of the tests were run with the slab open to the air we did check the effect of relative humidity. A cover placed over the slab caused the relative humidity to become very high (~100%); water condensed at many spots on the cover and the latices took four times longer to dry. By gently sweeping dry nitrogen over the latex surface we were able to obtain a comparatively low relative humidity (~0%) and the latices dried about four times faster than usual (in less than $\frac{3}{4}$ hr.). We examined three latices at the three relative humidities and observed no change in the MFT. These latices were samples I, IV, and X (see Table I). This result is different from the observation of Protzman and Brown⁶ in which a 2°C. change took place upon changing the relative humidity. However, a 2°C. change is the order of error observed in our experiments, and the difference between our results and that of Protzman and Brown is more apparent than real.

B. Particle Size Measurements

The particle size distributions and average sizes were determined by a sedimentation technique involving the use of an ultracentrifuge.⁷ The definitions of the various average radii used to characterize these latices are given in eqs. (1-4):

$$r_w = \sum w_i r_i = \sum_i n_i r_i^4 / n_i r_i^3 \quad (1)$$

$$r_s = \sum_i s_i r_i = \sum_i n_i r_i^3 / n_i r_i^2 \quad (2)$$

$$r_N = \sum_i n_i r_i \quad (3)$$

$$(r_H)^{-1} = \sum_i (n_i / r_i) \quad (4)$$

Here w_i , s_i , and n_i are the weight, surface, and number fractions, respectively, of the particles having radius r_i .

C. Surface Tension Measurements

The surface tensions of most of the latices were determined at their use concentrations by means of a Du Noüy ring tensiometer kept in the same constant temperature, constant humidity room as the MFT bar.

D. Torsional Modulus Measurements

A number of latices were coagulated by freezing (Dry Ice was dropped into a beaker containing the latex) after the emulsifier had been removed by

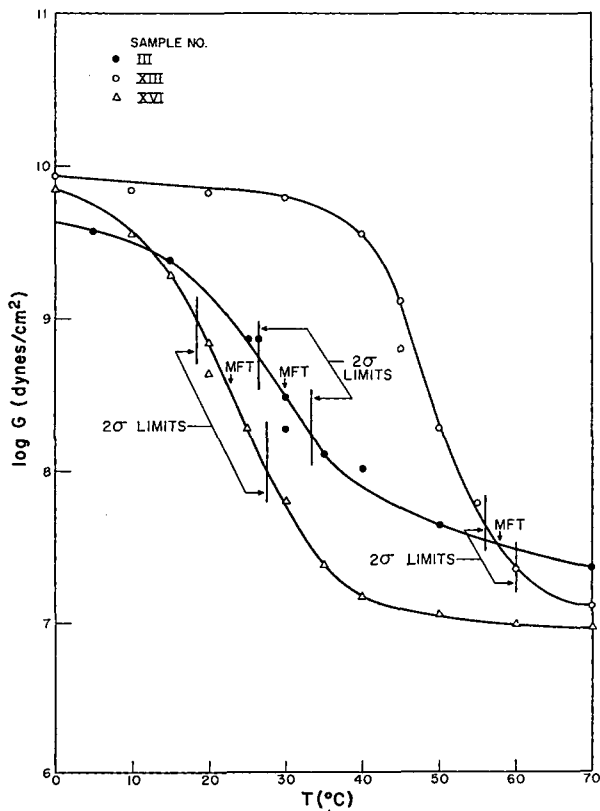


Fig. 1 Modulus as a function of temperature for three different polymer composition.

a mixed bed ion exchange resin. The coagulated polymer was then washed, dried, and pressed into a film under pressure at a temperature slightly above the glass temperature T_g of the polymer.

The torsional or shear moduli shown in Figure 1 were obtained with a torsion wire type of apparatus similar to Williamson's.⁸ A circulating fan and thermoregulator-controlled heaters were used for temperature control ($\pm 2^\circ\text{C}$). Dry Ice was placed in the cabinet to reduce the temperature.

The shear moduli shown in Figure 2 were obtained by a dynamic tester operating at a frequency of 0.055 cycles/sec.⁹ The temperature control chamber of this instrument permitted the wet polymer film to be under water throughout the test.

E. Latex Preparation

The polymerizations, in most cases, were carried out in a constant temperature bath. All the polymerizations were run in a prepurified nitrogen atmosphere after the reactants had been thoroughly degassed by bubbling the prepurified nitrogen through them for at least 1 hr.

The monomers were inhibitor-free and distilled where possible. Deionized water was used throughout. The emulsifier was sodium lauryl sulfate (Sipon WD) and the usual initiator was ammonium persulfate (Baker-

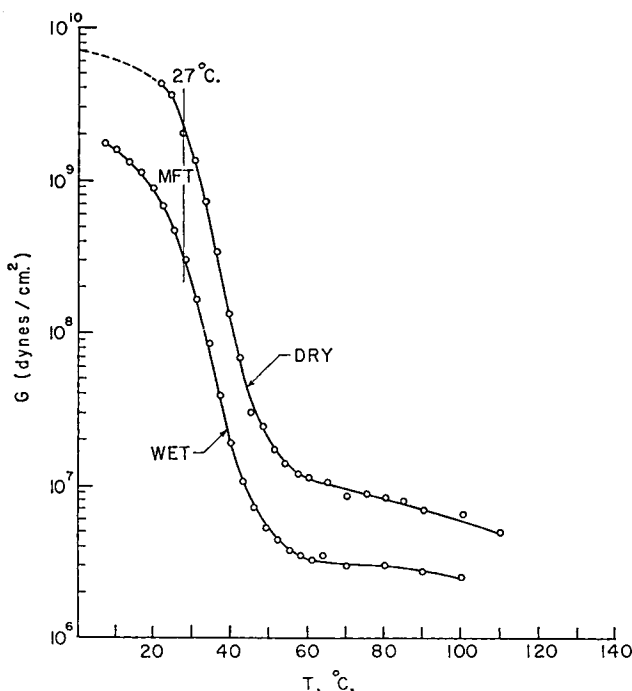


Fig. 2. Modulus as a function of temperature for air-dry and water-swollen films of 50% EA, 50% MMA.

Adamson Reagent Grade). In the redox recipes a trace of iron was used with technical grade sodium bisulphite and the ammonium persulfate.

The particle size was varied by changing emulsifier concentration or initiating system from thermal initiation to redox initiation. Such standard variations as monomer addition techniques and emulsion addition techniques were also used.¹⁰

F. Glass Temperatures

The glass transition temperatures of our samples were not measured but they were calculated from literature values of T_g for the homopolymers and the known weight fractions of the monomers used.¹¹

EXPERIMENTAL RESULTS

In Table I the MFT, volume-to-surface average radius r_s , harmonic average radius r_H , polydispersity index, r_w/r_n , and surface tension γ are listed for one homopolymer and three copolymer compositions. It can be seen that a large change in particle size, e.g., a factor of fifteen between the values of r_s for Samples I and V, does not appear to have much effect on the MFT. The data appear to scatter randomly with no obvious dependence on particle size. Assuming that in each latex type the differences observed are due to random errors, we obtain standard deviations σ which vary from

TABLE I
Effect of Particle Size on the Minimum Film Formation Temperature

Sample no.	Chemical composition of latex*	r_s, μ	r_H, μ	r_w/r_n	MFT, °C.	γ , dynes/cm.
I	nBMA	0.41	0.25	1.70	29	48
II		0.116	0.077	1.57	30	65
III		0.075	0.020	3.4	31	55
IV		0.063	0.040	1.62	32	57
V		0.027	0.011	2.5	28	61
VI	50% EA-50% MMA	0.118	0.019	5.5	25	58
VII		0.072	0.016	4.5	28	—
VIII		0.052	0.035	1.50	25	47
IX		0.034	0.0036	19.0	27	30
X		0.037	0.0026	20.0	30	46
XI	75% Styrene-25% nBA	0.050	0.0050	14.3	57	51
XII		0.049	0.0050	13.1	58	39
XIII		0.038	0.0101	4.6	59	46
XIV		0.024	0.0071	3.4	58	54
XV	55% Styrene-45% nBA	0.054	0.0062	13.5	25	43
XVI		0.045	0.0091	6.1	21	38
XVII		0.035	0.0091	4.0	25	40
XVIII		0.026	0.0046	5.2	21	43

* nBMA = *n*-butyl methacrylate, EA = ethyl acrylate, MMA = methyl methacrylate, nBA = *n*-butyl acrylate.

0.8 to 2.3°C. These are to be compared with a value of 0.9°C. calculated from the experiments of Protzman and Brown.⁶

We see in examining the change of shear modulus with temperature that the MFT is found in the region where the modulus is changing quite rapidly with temperature (Fig. 1). For the three illustrative curves shown on Figure 1 we have drawn in the 2σ limits, i.e., the region in which 95% of our MFT measurements would fall by pure chance. It is obvious that the variation of MFT due to random errors of measurement corresponds to a range in modulus which would easily compensate for the deliberate changes in particle size in testing the constancy of the ratio Gr/γ . Only for the nBMA latex III is the error in modulus less than the particle size change. Thus in general it is difficult to differentiate between experimental error and the lack of constancy of the ratio Gr_H/γ for a given latex type because of the rapid change of modulus with temperature.* Nevertheless, we did calculate values of Gr_H/γ for all the latices for which G was measured, and these values are tabulated in Table II.

TABLE II
Calculation of the Constant in the Brown Theory

Sample no.	MFT, °C.	$G \times 10^{-8}$ dynes/cm. ²	γ , dynes/cm.	$r_H \times 10^6$, cm.	Gr_H/γ
III	31	2.4	55	2.0	8.7
IV	32	1.2	57	4.0	8.4
VIII	25	35	47	3.5	260.0
XIII	59	0.27	46	1.01	0.58
XVI	21	5.4	38	0.91	12.9
XVIII	21	35	43	0.46	37.0

Although the differences in the value of Gr_H/γ between samples of the same type (III and IV or XVI and XVIII) are not significant in light of the variation of modulus within the limits of precision of the MFT measurement, the differences between types are definitely significant. Thus we must conclude that Gr_H/γ is a function of polymer type with the value increasing from 0.58 for a nonpolar copolymer (75% styrene-25% nBA) to a value of 260 for a more polar copolymer (50% EA-50% MMA). It should be noted that both extreme values are quite different from the predicted value of 35.²

According to Brown's theory the MFT is a function of the surface tension, increasing as the surface tension decreases if Gr_H/γ is to remain constant. Taking Sample V which had a high value of surface tension we added sodium lauryl sulfate to decrease the surface tension and measured the

* The radius r_H is used for comparison since the driving force is determined by the ratio γ/r for each group of spheres about a capillary. For a polydisperse latex we would sum these ratios giving $\sum n_i \gamma / r_i$ or γ / r_H to be equated to the resistance represented by G .

TABLE III
Effect of Added Emulsifier on the Surface Tension and the MFT

γ , dynes/cm.	MFT, °C.	MFT calculated, °C.
61	28	30
48	33	32
40	33	33

effect on the MFT. The results are given in Table III. The MFT has increased as predicted when the surface tension decreased. The order of magnitude of change is correct if we assume that the dependence of modulus on temperature is the same for both Samples III and V and that the average value of the MFT for all the nBMA latices, 30°C., is the one that should be observed for V (Table III).

In the picture of Barb and Mikucki a continuous film is formed at a pseudo second-order temperature which is characteristic for a large surface to volume ratio and lower than the glass temperature of the bulk material, T_g . Our results show no change of MFT with surface-to-volume ratio (Table I) and also the MFT may be above the T_g as well as below it (Table IV). However, the difference between the MFT and T_g appears to be a

TABLE IV
Correlation of Polarity of the Polymers with Measurable Parameters

Sample type	MFT, °C.	T_g , °C.	MFT- T_g , °C.	Gr_H/γ
75% Styrene-25% nBA	58	48	10	0.58
nBMA	30	22	8	8.5
55% Styrene-45% nBA	23	17	6	25.0
50% EA-50% MMA	27	30	-3	260.0

function of the polarity of the polymer, going from negative values to positive values as the polarity decreases. This agrees with the practical experience of formulators who observe that the MFT of weak acid containing copolymers decreases as the pH is increased, i.e., as the latices become less hydrophobic or more polar.¹² Plasticization by water is a possible explanation and it will be discussed below.

DISCUSSION

Our results indicate that the measurement of the MFT does not afford a critical test of the various film formation theories because of the lack of sufficient accuracy in the test method. Technologically, however, our results are important in that they show that the ability to form a film is not strongly dependent on particle size or surface tension and any attempt to control MFT by controlling those parameters, within limits, will fail. The mechanical properties of the system, i.e., the modulus-temperature char-

acteristics, are the predominant determinant of the MFT although the chemical composition of the polymer is obviously of some importance. In fact it appears that if two idealized polymers having the same modulus-temperature curves differed in polarity as much as the 75% styrene-25% nBA, and 50% EA-50% MMA copolymers, they would differ in MFT by as much as 13°C. even though they would have the same T_g .

One may also take the view that at the same MFT different polarities would indicate different T_g 's, moduli and possibly hardness of the formed continuous films. Thus, the more polar copolymer would form a film with a higher T_g and possibly a greater hardness. Three latices of approximately the same MFT ($\sim 19^\circ\text{C}$.) but different polarity were cast on glass at room temperature, and the Knoop Hardness Number (KHN) was determined by means of a Tukon microhardness tester. The experimental results given in Table V support the validity of our picture of the effect of polarity.

TABLE V
Correlation of Polarity of Polymers with Film Hardness at Constant MFT

Sample type	MFT, °C.	T_g , °C.	KHN
55% EA, 45% MMA	18	25	2.9
50% Styrene, 50% BA	21	10	1.25
Standard styrene-butadiene latex	18	—	0.38

The changes of the ratio, Gr/γ , and the quantity (MFT - T_g) with hydrophobicity may be due to the measurements of G and T_g with relatively dry polymer samples. The spheres being deformed in the film formation process are soaked with water and the polar copolymers may exhibit some effect of plasticization; both G and T_g would thus be lower giving a lower value of Gr/γ and T_g and in better agreement with the results obtained with the nonpolar copolymers.

On Figure 2 are some results on the effect of water on the mechanical properties of a 50% EA-50% MMA copolymer. The addition of water lowered the modulus by a factor of seven in the region of the MFT (Fig. 2) and lowered the T_g by about 4°C. as measured by the maximum in the mechanical loss peak. These results are in agreement with those of McLoughlin and Tobolsky,¹³ who found that upon drying a poly(methyl methacrylate) sample, i.e., removal of the equilibrium 1.5% water content, the modulus in the transition region increased from approximately 2×10^6 to 27×10^6 dynes/cm.², a factor of fourteen. For the value of Gr/γ of the 50% EA-50% MMA copolymer to be constant and equal to that of the 75% styrene-25% nBA, the modulus of the 50% EA-50% MMA copolymer would have to decrease by a factor of approximately 400 due to water plasticization. This is much greater than the change observed. Thus it seems that the plasticization of the polymer by water would not be enough

to account completely for the large differences observed. However, we do not know what effect the presence of emulsifier will have.

The absence of any observable effect when the time for film formation was varied by changing the relative humidity implies that an elastic response is acting as postulated by Brown.²

The theories other than Brown's have serious qualitative and quantitative objections. Brown's is consistent with the experimental data but it is obviously only a good first approximation, as Brown himself has acknowledged. Some changes to accommodate the dependence of the ratio Gr/γ on chemical compositions and the effect of different emulsifiers are now needed.

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Résumé

La température au-dessus de laquelle un latex polymérique forme un film continu, c.à.d. la température minimum de formation de film (désignée par MFT) a été étudiée en fonction de la dimension des particules, la tension superficielle et la rigidité du polymère. MFT se situe dans la région où le module du polymère G décroît rapidement avec une augmentation de température. MFT est indépendante des dimensions des particules et dépend très fortement de la rigidité du polymère. L'erreur statistique de mesure de MFT est toutefois équivalente à un changement de module du polymère du même ordre de grandeur que les variations de dimensions des particules. Le rapport Gr/γ , où r est le rayon des particules et γ la tension superficielle, peut ainsi être constant, comme prévu par Brown pour une composition chimique déterminée, mais l'instrumentation utilisée n'était pas suffisamment sensible pour le prouver. La valeur de ce rapport toutefois dépend nettement de la composition chimique, et varie d'une valeur moyenne de 0.58 pour un copolymère non-polaire (75% styrène, 25% acrylate *n*-butyle) à une valeur moyenne de 260 pour un copolymère plus polaire (50% acrylate d'éthyle, 50% méthacrylate de méthyle). La quantité (MFT- T_g) dans laquelle T_g est la température vitreuse des polymères, dépend également de la composition chimique, et varie de 10°C à -3°C, lorsqu'on passe d'un copolymère non-polaire à des copolymères plus polaires mentionnés ci-dessus.

Zusammenfassung

Die Temperatur, oberhalb welcher ein Polymerlatex einen kontinuierlichen Film bildet, das Filmbildungstemperaturminimum (abgekürzt MFT) wurde in Abhängigkeit von Partikelgrösse, Oberflächenspannung und Steifigkeit des Polymeren untersucht. Die MFT liegt in demjenigen Bereich, in welchem der Modul des Polymeren G mit steigender Temperatur sehr rasch abnimmt. Die MFT scheint von der Partikelgrösse unabhängig, von der Steifigkeit des Polymeren jedoch sehr stark abhängig zu sein. Der Versuchsfehler bei der MFT-Messung ist aber einer Änderung des Polymermoduls von der gleichen Grössenordnung äquivalent, wie die untersuchte Variation der Partikelgrösse. Es kann daher das Verhältnis Gr/γ , wo r der Partikelradius und γ die Oberflächenspannung ist, entsprechend der Voraussage von Brown für eine gegebene chemische Zusammensetzung konstant sein, die Empfindlichkeit der angewendeten Methode reichte jedoch zu einer Bestätigung nicht aus. Der Wert des Verhältnisses hängt hingegen in ausgeprägter Weise von der chemischen Zusammensetzung ab und bewegt sich von einem Wert von 0,58 für ein unpolares Copolymeres (75% Styrol, 25% *n*-Butylacrylat) bis zu einem mittleren Wert von 260 für ein stärker polares Copolymeres (50% Äthylacrylat, 50% Methylmethacrylat). Die Grösse $[MFT-T_g]$, wo T_g die Glas-temperatur des Polymeren ist, hängt ebenfalls von der chemischen Zusammensetzung ab und bewegt sich beim Übergang vom oben erwähnten unpolaren zum stärker polaren Copolymeren von einem Wert von 10°C bis zu -3°C.

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